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Chapter 1
Introduction

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1.1 Rubber in Engineering

Elastomers (natural and synthetic rubber) are amorphous polymers to which various ingredients are added, creating what the rubber chemist refers to as a compound. After heating and reaction (vulcanization), these materials become "rubber." Not only are they elastic and rubbery, but they also dissipate energy because of their viscoelastic nature. Their strength is high, especially under conditions of shear and compression. As with any mechanically loaded component, failure can occur as a result of fatigue. Thus, the long-term durability of rubber has to be predictable. Simple design criteria should be made available. Computer-aided design and analysis is desirable. Specifications are required to control product quality. Physical constants, as with any engineering material, should be readily available. These are the reasons for this book: *Engineering Design of Rubber Components.*

The next question is: which are the necessary chapters to read? Answer: all of them–sooner (the reason you probably bought the book) or later (the reason you are rereading the book), when you are having problems. Many failures of rubber components are best summarized as self-fulfilling prophecies. They are the result of a basic lack of understanding of the nature of rubber.

Rubber is an engineering material. Consider the process of designing a long-lived rubber component. To be successful, we must understand:

- Polymers and the rubbery state
- General design principles

This is not as daunting a task as it initially appears. Chapters 2 to 4 give background on polymers and the rubbery state, and Chapters 5 to 10 give some general design principles. Without attempting to preempt the authors, let me present a sometimes overly simplistic view that I might use in addressing a fellow engineer.

1.2 Elastomers

Elastomers are essentially supercondensed gases because most precursor monomers are gases. Their density is greater by approximately 3 orders of magnitude, and viscosity by 14 orders, than the gaseous state. Through polymerization, a long-chain molecule is created (the primary structure of any polymeric material). The molecules can be arranged in an amorphous (rubbery), glassy, or crystalline phase. Elastomers are typically categorized as amorphous (single-phase) polymers having a random-coil molecular arrangement.

After it is properly compounded and molded into an engineered product, the material at some point is subject to an external force. When a solid body is deformed, an internal reactive force called stress, acting across a unit area, tends to resist this deformation. The measure of deformation is called strain. Consider now Fig. 1.1, a tensile stress–strain diagram for three physical states of a polymer: glassy, crystalline, and rubbery. Glassy

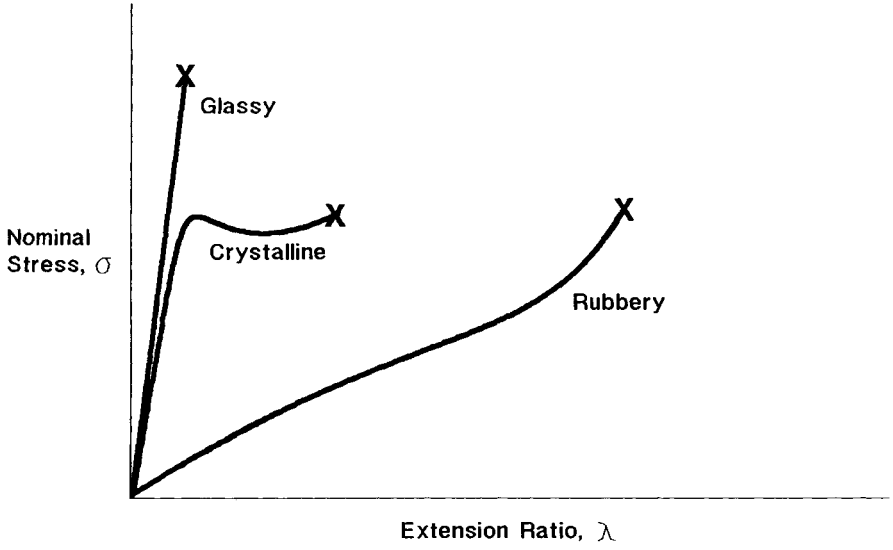

Figure 1.1 Tensile stress–strain diagrams for polymers in three physical states; X denotes rupture.

polymers are hard and brittle. The failure (rupture) point (X) is shown in Fig. 1.1. Crystalline polymers go through a succession of changes: elastic deformation, yield, plastic flow, necking, strain hardening, and fracture.

Rubber is unique in being soft, highly extensible, and highly elastic. Considering rubber as an engineering material, we can employ the term, shear modulus $G = NkT$, where N is the number of network chains, k is Boltzmann's constant, and T is temperature in Kelvins. With reasonable accuracy, we can state that many rubbery materials have a similar modulus G, or hardness, at equivalent temperatures above their glass transition temperature.

It is not inappropriate to look on rubber as a thermodynamic "system." In a static sense, it is an engineering material with a broad response to external influences, such as temperature and pressure. Of course, in reality, there is no such condition as a static application of rubber.

1.3 Dynamic Application

There are two basic mechanical properties of any material: modulus (stiffness) and damping (ability to dissipate energy). Typically, some energy is lost (converted to heat) in any deformation process. Viscoelastic response was originally modeled with a spring (elastic component) and dashpot (viscous response). For the spring, stress is directly proportional to strain (Hooke's law); for the dashpot, the rate of strain is proportional to the stress applied. Of course it is not that simple; a dashpot's resistance depends on

both time and viscosity. Consider a common example: a car shock absorber is stiff on a very cold day (high viscosity) and gives poor damping on a "washboard" road, at high frequency.

The rate at which a deformed elastomer returns to its original state after release is a function of its internal friction coefficient. This value ranges over many orders of magnitude. In butyl rubber, for example, it is very high, while for dimethyl silicone, it is very low. The time-temperature dependence of elastomers is of major importance, as discussed later.

1.4 General Design Principles

Rubber is an engineering material: this is a fundamental issue. To design adquately, basic mechanical properties must be appreciated.

Elastomers, as previously noted, are amorphous solids and behave isotropically (properties are independent of direction). The three elementary types of strain for isotropic materials are simple tension, simple shear, and uniform (hydrostatic) compression. The elastic behavior for these cases is defined by coefficients: Young's modulus E (tension), rigidity modulus G (shear), bulk modulus K (compression), and Poisson's ratio ν (see Chapter 3). Poisson's ratio, defined as the ratio of relative lateral contraction to longitudinal extension under a simple tension stress, is 0.5 for a totally incompressible solid. For elastomers, ν is 0.499 + (for steel, ν is approximately 0.3). For an isotropic incompressible material, $E = 3\ G$. The essential incompressibility of rubber has many consequences in design, manufacturing, and application.

1.5 Thermal Expansivity, Pressure, and Swelling

The coefficient of thermal expansion for elastomers is approximately 4.8×10^{-4}/K, similar to a hydrocarbon liquid. Addition of fillers reduces the value slightly. Comparing this expansivity to that of steel (3.5×10^{-5}/K), a tenfold difference, one begins to understand the built-in interfacial strains in a bonded rubber-metal or composite structure.

The high coefficient of expansion coupled with the high bulk modulus means that a potential exists for substantial thermal pressure if the elastomer is confined and subsequently heated. This describes the molding environment, with thermal pressure a necessity for replicating mold contours and surface finishes. The molding procedure of "bumping" vents excess rubber created by this thermal expansion. If not relieved, the thermal pressure could exceed the press clamping force. This can make the mold open at the parting line, creating a condition referred to as "back-rind." Beerbower [1] has calculated these pressures using the ratio γ of thermal expansion at constant pressure to compressibility at constant temperature. This value is available from the *Polymer Handbook* [2]. It is reasonable to use a value for γ of 1.13 for saturated backbone hydrocarbon elastomers (identified according to the American Society for Testing and Materials by

ASTM D 1418 designation "M"; e.g., EPDM) and 1.22 for unsaturated elastomers (ASTM D 1418 designation "R"; e.g., NBR, SBR, NR). Using Beerbower's equation:

$$P\,(\text{MPa}) = 0.1 + 298\,\gamma \ln\frac{T}{298} \tag{1.1}$$

it is possible to predict the pressure developed. For example, if an EPDM seal is completely confined at 25 °C (298 K), and the temperature is increased to 150 °C (423 K), the potential thermal pressure is 118 MPa (17,100 psi).

Thermal pressure and osmotic swelling pressure can be additive, but the terms should not be confused. Rubber components are often exposed to a liquid that has some degree of thermodynamic compatibility (partial solubility). When two liquids are mixed together, they can be (a) totally miscible (soluble), (b) partially miscible, or (c) totally immiscible. We avoid elastomer selections based on (a) unless we need to make a rubber solution. We prefer (c), but it is often difficult (high cost) or impossible. We must therefore learn to design with (b), partial miscibility. Going back to our design application, the rubber component can swell and the osmotic swelling pressure (3 to 500 psi) can be roughly calculated by referring to a physical chemistry textbook. Suppose the now-swollen rubber completely fills the available volume. Increasing temperature develops a thermal pressure based on 100% confinement of the elastomer.

1.6 Specific Applications and Operating Principles

Consider three specific applications of elastomers:

- Seals
- Vibration and shock absorption
- Load-bearing applications (bridge and building bearing pads)

The dynamic response is important in each case, but this discussion concentrate on seals, such as O-rings or shaft seals. Each design creates a range of challenges extending beyond the selection of the suitable elastomer. An O-ring, for example, consists of a toroidal rubber seal, with sealing effected by deflection of the seal cross-section. This creates an initial seal contact stress. Lindley's paper is an excellent reference [3]. The average design limits for rubber deformation are typically 15% in compression and 50% in shear. Although these limits appear to be conservative, consider them from another aspect. Ferry (4) makes the following comments:

In considering the effectiveness of an elastomeric seal, two useful questions are:

1. After a sudden stress due to a change in articulation of the structure or a burst of pressure, how long will it take for the elastomer to adjust its shape to maintain the seal?
2. If there are oscillating stresses, will there be sufficient time in the period of oscillation for the elastomer to adjust its shape to maintain the seal?

Ferry's two questions are applicable to any seal, but they are particularly relevant to O-rings and lip-type shaft seals. Points 1 to 3, and the two paragraphs that follow are quoted from Ferry's memorandum [4].

1. Response to a sudden, transient shear stress is described by the creep compliance $J(t)$ or ratio of time-dependent strain to the applied stress. It depends on the time t elapsed since imposition of stress, as shown in Fig. 1.2 for a crosslinked elastomer. At short times, the shape change will be incomplete. For purposes of illustration, we will assume that accomplishment of 90% of the final shape change is satisfactory and indicate the corresponding time $t_{0.9}$ as shown in Fig. 1.2. It may be anywhere from milliseconds to hours, depending highly on temperature as well as the chemical nature of the elastomer and the degree of crosslinking.
2. Response in shape change to an oscillating stress can be described by the storage shear compliance J', but a more familiar property is the storage shear modulus G', or the ratio of the elastic (in-phase) component of stress to the oscillating strain (see Chapter 4). It varies with frequency, as shown in Fig. 1.3 for a crosslinked elastomer. At high frequencies, the elastomer will appear to be stiff and the shape changes will be incomplete. Similarly, we assume that an increase in stiffness of 10% will be satisfactory and indicate the corresponding frequency $f_{1.1}$ as shown.
3. Interrelation of $t_{0.9}$ and $f_{1.1}$ and their determination. For practical purposes, only one of the experiments of Figs. 1.2 and 1.3 needs to be performed to characterize the material. It can be estimated that

$$f_{1.1}\ (\text{Hz}) \cong \frac{0.2}{t_{0.9}}\ (\text{second}) \tag{1.2}$$

so one can be estimated from the other. If the elastomer is any good at all, $t_{0.9}$ should be very small and the experiment of Fig. 1.2 is not practical. The usual test would therefore be of the dynamic shear storage modulus G' (or the corresponding Young's modulus, $E' = 3G'$). The test usually needs to be performed at only one temperature, T_o, since values at any other temperature can be calculated from the shift factor a_T (as discussed in Chapter 4). The temperature dependence of a_T depends primarily on the chemical nature of the elastomer. Data are available in the literature for many elastomers.

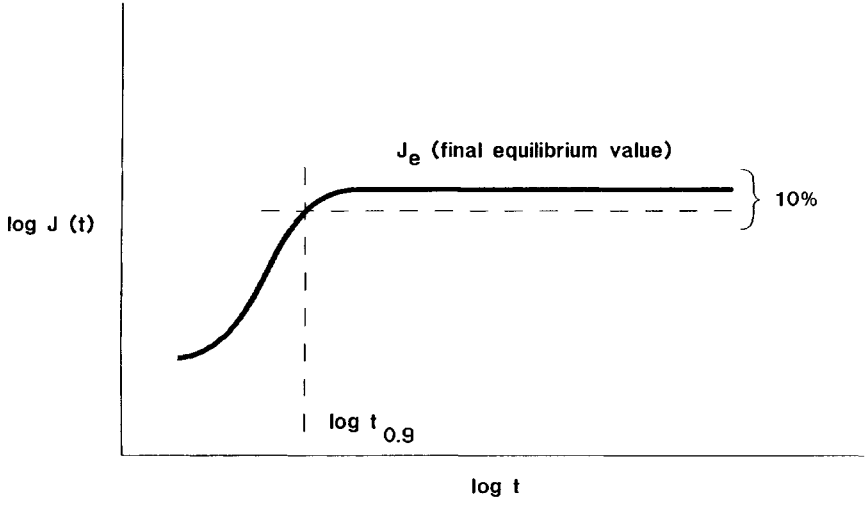

Figure 1.2 Schematic diagram showing response (compliance J) as a function of time.

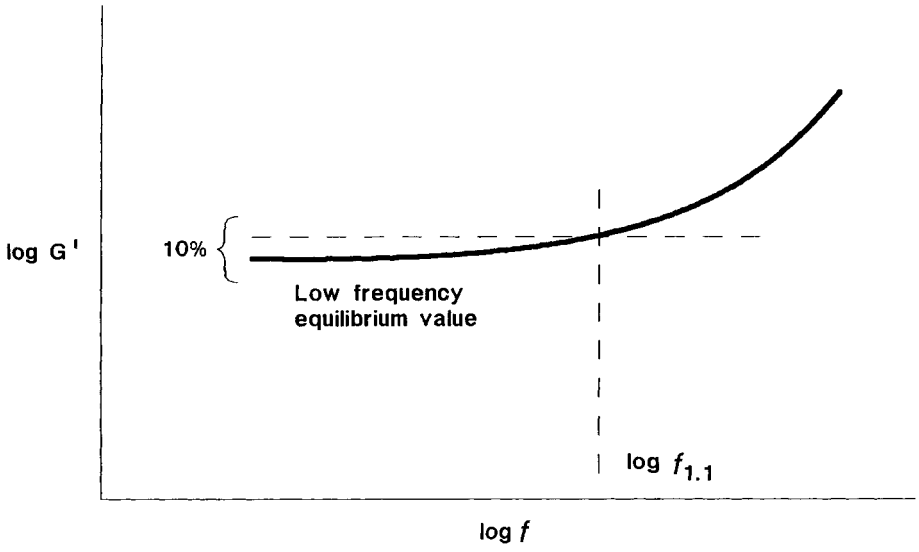

Figure 1.3 Schematic diagram showing real part G' of dynamic shear modulus as a function of frequency f.

The examples given in Table 1.1 for cured 1,4-polybutadiene and butyl rubber were evaluated by the procedure illustrated in Fig. 1.2 with the use of Eq. (1.2) to obtain $t_{0.9}$, at 25 °C. The values at −25 °C were obtained from Eq. (1.2) with values of log a_T taken from the literature: 1.32 for polybutadiene, and 2.98 for butyl rubber.

According to these estimates the response to transient stress would be very rapid for polybutadiene at both temperatures, and a frequency of 13 Hz could be tolerated even at −25 °C without exceeding a 10% rise in G'. For butyl rubber, well known to have slower responses, the response appears barely satisfactory at 25 °C, but at −25 °C, a 40 second requirement for a transient stress and a maximum frequency of 0.005 Hz for oscillatory stress would probably be unacceptable.

Thus, the key to leak-free sealing is a rapid recovery of the seal deformation. Having determined the natural recovery time, we convert the imposed (disturbing) frequency f into a real time interval $t = 1/2\pi f$. If the ratio of recovery time to real time exceeds 1, then the seal will leak. If it is about 1, the seal might leak, because of resonance, and if it is less than 1, the seal should not leak.

Table 1.1 Characteristic Response Times and Frequencies

	1,4-Polybutadiene		Butyl rubber	
	25 °C	−25 °C	25 °C	−25 °C
$t_{0.9}$, s	0.0008	0.015	0.04	40
$f_{1.1}$, Hz	250	13	5	0.005

1.7 Seal Life

Seal life in dynamic applications is strongly dependent on the development of a hydrodynamic film between the rubber surface and the sealing surface. The ability of a lubricant to wet these surfaces is a function of their surface chemistry. The long life of a rubber marine "cutless" bearing is enhanced by the use of nitrile rubber, probably because the polar aspect of the nitrile groups creates a high energy, easily wetted surface. Conversely, the low abrasion resistance of a silicone rubber shaft seal is probably due, in part, to the low energy surface of silicone rubber, which tends to discourage "wetting" of the elastomer by the lubricant.

1.8 Seal Friction

Roberts [5] notes that the coefficient of friction of rubber ranges from 0.001 to 10 depending on the interface conditions. In the case of a shaft seal or O-ring, a typical hydrodynamic film thickness is about 150 nm. Shearing of this film is the prime cause of dynamic or running friction, so that the dynamic coefficient of friction is a function of lubricant viscosity and sliding velocity. The coefficient generally starts high, because seal contact stress breaks down the hydrodynamic film, then decreases to a minimum value as the sliding velocity is increased, and then increases again. Thus, running friction can be minimized by optimizing viscosity and velocity effects.

Seal friction creates a heat buildup, often causing premature failure due to excessive heat aging of the elastomer. Early nitrile seal formulations often included a high percentage of graphite as a filler. One might assume that graphite was used to reduce friction. In actuality, it increased the thermal conductivity, thus carrying heat away from the rubbing surface. Graphite is no more than a bulk filler (increasing hardness only), offering little or no reinforcing capabilities on its own. Today's trend is to utilize finer-particle, reinforcing, furnace-type carbon blacks. Concurrent with this change, engine oil temperatures have increased with smaller engines operating at higher rpm's. This combination of more severe operating conditions and changing seal requirements has forced seal manufacturers to use more temperature-resistant elastomers. A conventional nitrile (NBR) elastomer might be capable of meeting the static heat-aging requirements at oil operating temperatures (now 135 to 150 °C). But the additional thermal load created by seal friction can raise this value to 175 to 200 °C at the seal contact area, a temperature in excess of the capabilities of nitrile rubber. Finite element modeling (FEM) of heat transfer in rubber products is increasingly needed in the design stage, using a specific heat value of the rubber compound to maximize service life.

1.9 Acknowledgments

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1.10 References

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